

UNITED STATES DEPARTMENT OF AGRICULTURE
 Agricultural Research Administration
 Division of Agricultural and Industrial Chemistry

BUTYL ACRYLATE-ACRYLONITRILE RUBBERS RESISTANT TO HEAT,
 OILS, AND LOW TEMPERATURES

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BUTYL ACRYLATE-ACRYLONITRILE RUBBERS RESISTANT TO HEAT, OILS, AND LOW TEMPERATURES*

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Substantial evidence now exists in published data on high polymers which demonstrates that many polymers and copolymers of alkyl acrylates can be vulcanized by a number of curing recipes (1-9). Outstanding among such polymers and copolymers from the commercial viewpoint, are the ethyl acrylate polymer Hycar PA (5), and the ethyl acrylate-chloroethyl vinyl ether copolymer Lactoprene EV (3,4,6,8) now being produced with commercial modifications as Hycar PA-21 and Hycar PA-31 (5). When these materials are cured with suitable recipes, vulcanizates are produced, which among other desirable properties, have outstanding resistance to hot petroleum base oils.

Acrylic vulcanizates, in addition to Hycar PA and Lactoprene EV, which have been described as having superior heat and oil resistance include copolymers of ethyl acrylate with chloropropyl acrylate (6). The great majority of copolymers reported as vulcanizates were cured with recipes which produced inferior heat resistance. The recipes employed were designed to evaluate tensile properties and curing characteristics rather than to produce compositions having superior heat resistance. Consequently, it should not be assumed that the inferior heat resistance of these compositions was inherent in the copolymers themselves, or that improved heat resistance could not have been obtained with a different curing recipe.

Recent results obtained with copolymers of n-butyl acrylate and acrylonitrile demonstrate that with certain amine curing recipes, vulcanizates can be obtained which compare favorably in heat resistance with similar compounds of Lactoprene EV. The utility of acrylonitrile as a functional part of the polymer chain is apparently not limited to its apparent role in vulcanization. When thus copolymerized with n-butyl acrylate, the acrylonitrile also serves to modify the tensile properties and solubility characteristics of the copolymer without causing excessive brittleness at low temperatures.

To conform with earlier developments of this Laboratory in the field of vulcanizable acrylic copolymers, these butyl acrylate-acrylonitrile copolymers, as a class, are designated Lactoprene BN. The designation is followed by a number, as for example, Lactoprene BN-10 to indicate the percent of acrylonitrile in the monomer mixture which was used in preparing the copolymer.

* PRESENTED AT FOURTH MEETING-IN-MINIATURE OF THE PHILADELPHIA SECTION OF THE AMERICAN CHEMICAL SOCIETY ON JANUARY 18, 1951.

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EXPERIMENTAL

Copolymers of butyl acrylate and acrylonitrile were prepared by emulsion polymerization under nitrogen at 80° C., using the following recipe:

| | |
|--------------------------|-------|
| n-butyl acrylate | 100-x |
| acrylonitrile | x |
| distilled water | 200 |
| emulsifier (Dupanol ME) | 2.5 |
| Catalyst ($K_2S_2O_8$) | 0.01 |

The monomers, emulsifier, and water were mixed and brought up to 80° C. The catalyst was then added and polymerization began within a few minutes thereafter. Polymerization was approximately complete within 2 to 3 hours at 80° C. The emulsion was coagulated in a mixture of ethanol, water and hydrochloric acid in a volume ratio of 5:5:1, washed with distilled water three times, and dried in a circulating air oven at 40° C. for 24 to 72 hours or until no appreciable odor of monomer was apparent. Conversions were of the order of 80 percent.

Later results on the polymerization of these copolymers obtained in this Laboratory (10) have demonstrated that: the use of nitrogen as a polymerization atmosphere is unnecessary above 80° C.; the use of supplementary catalyst added during the course of the polymerization serves to increase the conversion to 95-98 percent without adversely affecting the properties of the resulting copolymer; and other more economical methods for coagulating the latex such as alum precipitation may be used effectively.

The copolymers were compounded, cured and tested in accordance with standard ASTM procedures. In each case, the crude copolymer was masterbatched with the SRF black and the stearic acid in a hot Banbury mixer. The batch was usually mixed for a total time of six minutes at slow speed with the ram down, and was dumped at a temperature approximately 350° F. After the masterbatch cooled, it was sheeted on a warm 2-roll mill.

The sulfur and triethylene tetramine were added on the mill. It was observed when milling the 90 butyl acrylate-10-acrylonitrile stock, for example, that the amine could be added slowly and continuously without causing the band to break or to migrate to the back roll. With small amounts of the amine such as 1 to 2 parts per 100 of copolymer by weight, the compounded stock could be refined by passing through tight rolls at 160-170° F. without tending to stick to the rolls or becoming tender. The higher the amount of acrylonitrile in the copolymer, the more readily could the stock be refined. The 90 butyl acrylate-10-acrylonitrile compounded stock exhibited considerably less shrinkage on the mill than did similar compounds of Lactoprene EV. Further, it appeared smoother and more glossy than the EV compounds. These observations suggest that the butyl acrylate-acrylonitrile compositions may have inherently better processability than ethyl acrylate copolymer compositions. Most of the subject copolymer compositions were cured for 60 minutes at 298° F. for test purposes.

RESULTS

Tensile property data obtained on green and heat-aged (350° F. for 72 hours) samples, together with Mooney viscosities of the raw copolymers and brittle points, compression set, and swelling data of the vulcanizates, are shown in Table I. The ratios of butyl acrylate to acrylonitrile indicated at the top of each column are actually the concentrations of the monomers used in the polymerization. Nitrogen analyses from later experiments (10) indicate that the copolymers are usually somewhat richer in the ester than the monomer ratio would indicate. It will be observed that both the brittle point and the curing rate of the copolymers increase with increasing acrylonitrile content. Additional data on differential swelling in organic solvents which substantiate this direct relationship between the state of cure and the acrylonitrile content will be presented in a forthcoming publication. Sulfur was omitted from the 100 percent butyl acrylate control stock because it tends to retard cure. However, its use in the butyl acrylate-acrylonitrile compositions is desirable for superior heat resistance.

The copolymer prepared from a monomer mixture of 87.5 percent butyl acrylate and 12.5 percent acrylonitrile was selected for further study. Its initial hardness and brittle point, together with the effect of aging in hot air and in hot ASTM No. 3 oil on hardness, brittle point, and weight are shown in Table II. The reader will observe that on the basis of equal loading, the weight increase of the butyl acrylate copolymer in the hot oil was somewhat greater than that of the ethyl acrylate copolymer. However, this moderate swell is within specification requirements for oil resistant gasket rubbers and, in comparison with ethyl acrylate rubbers, possesses the advantage of lower brittle point. Of course, as is well known, the unsaturation of the diene rubber control makes it unsuited for exposure to hot oils containing sulfur.

The swelling of the butyl acrylate copolymer in hot oil could be reduced further, obviously, by increasing the percentage of acrylonitrile in the copolymer, an improvement to be had at sacrifice of low temperature flexibility.

The reader will also note that the butyl acrylate copolymer in Table II was cured at 350° F. while the ethyl acrylate control was cured at 298° F. The butyl acrylate copolymer was cured at the higher temperature in an attempt to improve cure to the point where a "temper" in a hot air oven following cure would be unnecessary for maximum compression set resistance. Had the butyl acrylate stock in the table been cured, as others were, for 60 minutes at 298° F., the properties would not have differed appreciably from those shown.

The properties of Lactoprene BN vulcanizates classify them as specialty rubbers rather than general purpose rubbers. Because of their combined resistance to hot oils, dry heat, water, and low temperatures they should provide improved materials for the manufacture of oil seals, coolant seals, O-rings, gaskets and similar mechanical specialties.

Table I. Properties of n-Butyl Acrylate-Acrylonitrile
Copolymers Containing Variable Amounts of Acrylonitrile

| | Copolymer Composition, % | | | | |
|--|--------------------------|------------------|--------------------|--------------------------|--------------------|
| | 100 - 0 | 95 - 5 (BN-5) | 90 - 10 (BN-10) | 87.5 - 12.5 (BN-12.5) | 85 - 15 (BN-15) |
| Raw Mooney, ML-4, 212° F. | 21 | 25 | 29 | 37 | 44 |
| Recipe | | | | | |
| Copolymer | 100 | 100 | 100 | 100 | 100 |
| Stearic Acid | 1 | 1 | 1 | 1 | 1 |
| Sulfur | - | 0.67 | 0.5 | 1.0 | 0.67 |
| Triethylene tetramine | 2 | 1.3 | 1.0 | 1.0 | 1.3 |
| SRF black | 50 | 50 | 50 | 50 | 50 |
| Cure (minutes/° F.) | 60/298° | 60/298° | 60/298° | 60/298° | 60/298° |
| Initial Properties | | | | | |
| Tensile strength, psi | 490 | 810 | 1360 | 1400 | 1590 |
| Ultimate elongation | 920 | 640 | 250 | 280 | 240 |
| Modulus at 100%, psi | 45 | 150 | 340 | 290 | 470 |
| Durometer, 30 sec. | - | - | 55 | 54 | 60 |
| Volume change, %, after 48 hrs. at 212° F. in water | - | - | 6.0 | 6.0 | - |
| Volume change, %, after 48 hrs. at 72° F. in iso-octane | - | - | 23 | 18 | - |
| Volume change, %, after 2 weeks at 72° F. in Circo Light Process Oil | - | 16. | 10 | 8 | 2 |
| Compression Set, 70 hrs. at 250° F (ASTM Method F) | - | 77 ^a | 70 ^a | 66. | 66 ^a |
| Compression Set ^b , 70 hrs. at 250° F. (ASTM Method B) | - | 35 ^a | 31 ^a | - | 31 ^a |
| Brittle Point, ° F ^c | -56. | -42 | -36. | -22 | -15 |
| Aged Properties, 72 hrs./350° F. | | | | | |
| Tensile strength, psi | soft | 720 | 1240 | 1310 | 1600 |
| Ultimate elongation, % | - | 360 | 140 | 120 | 100 |
| Modulus at 100%, psi | - | 50 | 800 | 1100 | 1600 |
| Durometer, 30 sec. | - | - | 67 | 70 | 79 |

^a Recipe, 1 part sulfur and 1 part triethylene tetramine.

^b Samples previously tempered in air for 24 hrs. at 350° F.

^c ASTM Method of Test D746-44T, manually operated.

Table II. Brittle point and hot oil resistance of a butyl acrylate-acrylonitrile copolymer compared with an ethyl acrylate-chloroethyl vinyl ether copolymer and a butadiene-acrylonitrile copolymer.

| Copolymer | butyl acrylate ^a acrylonitrile | ethyl acrylate ^b chloroethyl vinyl ether | butadiene- ^c acrylonitrile |
|--|--|---|--|
| Composition, % | 87.5-12.5 | 95 - 5 | 75 - 25 |
| Recipe | | | |
| Copolymer | 100 | 100 | 100 |
| Zinc oxide | - | - | 5 |
| Stearic acid | 1 | 1 | 1 |
| SRF black | 50 | 50 | 75 |
| Sulfur | 0.67 | 1 | 1.5 |
| Triethylene tetramine | 1.3 | - | - |
| Trimene Base | - | 4 | - |
| Benzothiazyl disulfide | - | - | 1 |
| Cure (minutes/°F.) | 30/350° | 60/298° | 60/287° |
| Properties, initial | | | |
| Durometer, 30 sec. | 46 | 61 | 65 |
| Brittle point, °F. ^d | -22 | +23 | -53 |
| Properties, aged in air 68 hrs./300°F. | | | |
| Durometer, 30 sec. | 54 | 65 | 90 |
| Brittle point, °F. ^d | -18 | +25 | +70 |
| Change in weight, % | -1.6 | -1.7 | -1.1 |
| Properties, aged in ASTM No. 3 oil 68 hrs./300°F. | | | |
| Durometer, 30 sec. | 30 | 61 | 27 |
| Brittle point, °F. ^d | -27 | +18 | -60 |
| Change in weight, % | +27.6 | +9.5 | +41.6 |

^a Lactoprene BN-12.5

^b Lactoprene EV

^c A commercial nitrile rubber

^d Modified ASTM Method of Test, D746-44T, solenoid operated.

ACKNOWLEDGMENT

The authors are indebted to the Delaware Research and Development Corporation for the properties data of Table II; to E. M. Filachione and T. J. Fitzpatrick for reference to unpublished experiments dealing with copolymerization; and to W. E. Palm and H. C. Fromuth for assistance in the experimental work

LITERATURE REFERENCES

1. MAST, W. C., REHBERG, C. E., DIETZ, T. J. AND FISHER, C. H., IND. ENG. CHEM. 36: 1022 (1944).
2. MAST, W. C., SMITH, LEE T., AND FISHER, C. H., IND. ENG. CHEM. 36: 1027 (1944).
3. MAST, W. C., DIETZ, T. J., AND FISHER, C. H., INDIA RUBBER WORLD 113: 223 (1945).
4. DIETZ, T. J., MAST, W. C., DEAN, R. L. AND FISHER, C. H., IND. ENG. CHEM. 38: 960 (1946).
5. B. F. GOODRICH CHEMICAL CO., SERVICE BULLETINS 47-SD3- (1947) AND H-6 (AUG. 1950).
6. MAST, W. C., DIETZ, T. J., DEAN, R. L., AND FISHER, C. H. INDIA RUBBER WORLD 116: 355 (1947).
7. MAST, W. C. AND FISHER, C. H., IND. ENG. CHEM. 40: 107 (1948).
8. HANSEN, J. E., PALM, W. E., AND DIETZ, T. J., BUR. AGRIC. AND INDUSTRIAL CHEM., EASTERN REG. RES. LAB., AIC-205 (SEPT. 1948). PROCESSED.
9. MAST, W. C. AND FISHER, C. H., BUR. AGRIC. AND INDUSTRIAL CHEM., EASTERN REG. RES. LAB., AIC-206 (DEC. 1948). PROCESSED.
10. FILACHIONE, E. M., ET AL., UNPUBLISHED DATA (1950).